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THE AIR AFTERGLOW REVISTED

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THE AIR AFTERGLOW REVISITED

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A. INTRODUCTION

To begin with a little soul-searching: the fact that science and technology are advancing at an ever accelerating rate, while both the number of investigators working in a given field and their level of support are at best levelling off, has put us in a new bind. Blessed with marvellous gadgets of all types, photomultipliers capable of detecting a few light quanta, tunable lasers of great power, narrow spectral width, and ultrashort repetitive flash duration, with ultrahigh vacuum techniques and ultrafast time resolution, with a bulging arsenal of analytical methods for measuring neutral or charged species in specific quantum states, etc., etc., our ability to study physical and chemical processes ever more minutely appears to be without limit. This widens immensely the discrepancy between what is doable technologically and what can actually be undertaken, particularly when we remember how expensive most of our new 'toys' are. The bind is, then, the increasing selectivity which we must exercise in our choice of systems and problems to work on, since neither the 'Everest' justification ('because it is there') nor the 'Part XXIV in a series of continuing studies' justification is quite good enough.

Serendipitously, it turns out that the air afterglow - the O + NO chemiluminescence - is a fine example of a system well worth studying for many reasons ranging from environmental and societal to purely scientific. Very

briefly, these are as follows:

(1) The phenomenon is observed in the normal and perturbed upper atmosphere[1] where its potential usefulness in measuring the local or column integrated [O] [NO] product has not yet been fully realized;

(2) It is an extremely sensitive monitor of either O- or NO- concentrations wherever one or the other is known and has therefore been successfully used in laboratory O-atom kinetic studies[2] for about 15 years, but is equally applicable to NO measurements in combustion and pollution studies, where it may sometimes be preferred over its much more weakly emitting sister-reaction, O_3 + NO;

(3) Following the work of Fontijn, Meyer, and Schiff,[3] it has become a secondary actinometric standard for the study of other glows in the visible or near ultraviolet, a function which is now being expanded in our laboratories to the infrared; and

(4) As a fundamental chemiluminescent system it is one of the best characterized, most thoroughly studied, and represents an opportunity to analyze and resolve in a small system the increasingly insoluble problems of larger molecules. The present review will first attempt to bring the reader up to date on the recent results of direct experimental studies and then to discuss and interpret these results in the light of supporting work on the spectrum, fluorescence, photodissociation, and quantum theoretical calculations of NO_2.

B. REVIEW OF EXPERIMENTAL RESULTS

B. 1. The Pressure Dependence

The once raging battle whether the O + NO chemiluminescence is a truly bimolecular radiative recombination whose rate constant, $I_0 \equiv I/[O] [NO]$, is pressure independent or whether it is principally a termolecular process at its high pressure limit (even at as low a pressure as 1 Torr because of the long

radiative lifetime of NO_2^*) which requires I_0 to fall off with decreasing pressure; this battle is now ended. I_0 does decrease, but does not do so indefinitely. It apparently levels off again at very low pressures ($\leq 10^{-4}$ torr) in what appears to be a compromise solution of the problem, albeit one which requires about 90% termolecular and only 10% bimolecular character. This experimental result is much more satisfactorily represented by a model which involves the bimolecular formation of an unstabilized NO_2^* collision complex followed by vibrational energy transfer within NO_2^*, electronic energy transfer to ground-state NO_2, (both of them collisional processes), or spontaneous radiative decay to NO_2, with the exact nature of NO_2^* to be discussed later.

The experimental basis for this interpretation is shown in Fig. 1 which shows an approximate summary of all work on pressure-dependence on a logarithmic pressure scale, arbitrarily normalized (and extended) to "high" pressure. Its chronology is not without irony. In 1964, both Harteck's[4] and Jonathan's[5] groups reported pressure independence down to 3 millitorr, but this was challenged by Kelso and myself[6] on the basis of experiments in a 2.5 cm diameter flow tube down to 30 millitorr. A few additional experiments of Harteck's group[7] seemed to confirm the pressure independence, but Jonathan and Petty's[8] measurements in flow tubes of 2.5, 5.0, and 12 cm diameters clearly showed a fall-off in I_0. On the other hand, our early measurements undoubtedly overshot the mark, i.e. showed too large a fall-off due to diffusion and surface recombination effects. All other recent studies have shown good agreement on the decrease of I_0 with decreasing pressure. McKenzie and Thrush[9] studied pressure and M-effects from 10 to 100 millitorr and their points in Fig. 1 were obtained from their Stern-Volmer type expression (they refer to Ar carrier gas whereas all others refer to $M=O_2$), and the extensive work of Becker et al,[10,11] first in a 200 liter and then in a 2×10^5 liter sphere, and that of Cody[12] in my laboratory

span the much larger pressure range of 0.1 to 100 millitorr.

Our data were obtained in a 15 cm diameter flow tube pumped by any suitable combination of forepump (15 lit/sec), Roots blower (130 lit/sec), and 6 inch oil diffusion pump (about 700 lit/sec with cooled baffle). The emission was viewed by a cooled photomultiplier through any one of 12 interference filters from 4050 to 7850Å, 6 of which could be mounted on a filterwheel. The O-atom concentration was measured by resonance absorption near 1300Å across the flow tube at the same axial position where the chemiluminescence signal was obtained in order to avoid assumptions regarding the catalytic behavior of surfaces over large pressure ranges. Fig. 2 shows a schematic diagram of the apparatus.

The points plotted in Fig. 1 should have variable but reasonably large error bars ($\pm$ 10 to 30%) attached to them, but it is abundantly clear that a substantial fall-off exists and that the two most extensive studies, at Bonn and Pittsburgh, are in excellent agreement. It should also be said that only the points and curve of Becker, Groth, and Thran[11] represent I_0 values, properly integrated across the emission spectrum, but since substantially smaller fall-off ratios only occur at the blue end of the spectrum (see B. 3. below) which contributes relatively little to the total emission, the comparison of Fig. 1 is valid.

B. 2. The M-Dependence

This question is complementary to that of the pressure dependence, because, in a truly bimolecular recombination, there is, of course, no M-effect, and in a termolecular one (or in a vibrational energy transfer sequence) it would be astonishing and improbable if there were none. It should be emphasized, however, that large M-effects would be unlikely, since one really observes the ratio of two M-effects, that for the termolecular formation of an NO_2^* (or its

vibrational relaxation in the energy transfer mechanism) to that for electronic quenching of NO_2^*, and although it is unlikely that the relative efficiencies of different M should be the same in the two processes (leading to no effect) it is also likely that, for the simple atoms and molecules investigated, there should be some parallelism and partial cancellation leading to small M-effects.

Experimental data are shown in Table I which includes our earlier results and various other entries. Surprisingly good agreement abounds, when one considers the small magnitude of the relative effect, except for the results of ref. 7 which show no M-effect as well as no pressure dependence. The entries for ref. 11 are their normalized d/q ratios for $\lambda=4450$Å and for 5600 or 6320Å where a second value is given. If the truly bimolecular part of I_0 and the radiative lifetime of NO_2^* are considered constant in these experiments, d/q equals the ratio of k_D^M, the termolecular rate constant for the formation of NO_2^* to its quenching rate constant, k_q^M. The results of McKenzie and Thrush[9] also lend qualitative support to the findings of an M-effect as, for example, in the ratio I_0 (green)/I_0 (blue) which, when normalized as $p \to 0$, approaches high pressure values in the order $Ar > O_2 > CO_2$, N_2O, $CH_4 > SF_6$.

TABLE I

Relative Emission Efficiencies, $R^M \equiv I_0^M/I_0^{O_2}$

M	Ref. 6	Ref. 7	Ref. 11 (a)	Other Work
He	1.25	1.03	1.28, 1.30	1.25[13]
Ne	--	--	1.20	
Ar	1.06	1.06	1.08	1.0[13]
N_2	1.15	--	1.10	
H_2	--	--	1.12	

TABLE I (continued)

Relative Emission Efficiencies, $R^M \equiv I_0^M / I_0^{O_2}$

M	Ref. 6	Ref. 7	Ref. 11 (a)	Other Work
CO_2	0.79	1.03	0.74, 0.79	0.75[8]
N_2O	0.86	1.02	--	
CH_4	0.7	--	--	
CF_4	0.50	1.02	--	
SF_6	0.52	--	0.52, 0.51	
H_2O	0.57	--	--	

(a) First value: $\lambda = 4450\text{Å}$; second value: $\lambda = 6320\text{Å}$ (He), $\lambda = 5600\text{Å}$ (CO_2, SF_6)

B. 3. The Spectral Dependence on p and M

Recent data of the pressure shift of the emission spectrum and of fairly monochromatic fall-off measurements which provide $I_0^\lambda(p)$ over a wide pressure range represent the clearest proof for the correctness of the termolecular/ energy transfer mechanism. This was first shown qualitatively by Freedman and Kelso[14] in my former laboratory, then by McKenzie and Thrush,[9] and in much greater detail by Becker et al[11] and by Cody.[12] The overall spectrum shifts towards the blue with decreasing pressure, i.e. although the spectral threshold remains unchanged, the relative intensities increase at the short wavelength end and decrease at long wavelengths. There is a concomitant change in the fall-off characteristics of $I_0^\lambda(p)$ - which is also a function of M, such that there is increasing fall-off as λ is increased from its threshold near 3970Å, as predicted by the energy transfer mechanism, since NO_2^* molecules which have lost some of their vibrational energy can not emit radiation at the blue end of the spectrum. Conversely, the emission very close to 3970Å must come mainly

from unstabilized NO_2^* and should therefore show no fall-off. This is supported by the recent data of Becker et al[11] and of Cody[12] as shown in Table II. Considering the very different experimental techniques, the agreement is very good.

TABLE II

Fall-off Ratios, $I_0^\lambda(p\to\infty)/I_0^\lambda(p\to 0)$
as Function of Wavelength for $M=O_2$

λ, Å

3980	4030	4050	4360	4450	4700	5360	5600	5660	6320	7250	Ref.
1.56	2.13	--	--	4.52	--	9.1	10.5	--	13.5	--	11
--	--	1.5	4.5	--	5.5	--	--	7.9	--	9.6	12

The data of Becker et al are probably more accurate, but the discrepancy at the long wavelength end is due at least partly to the manner of extrapolation from the highest pressures used in these experiments, which was near 100 millitorr in both studies, to $I_0^\lambda(p\to\infty)$ which should be reached near 1 torr. This amounted to 25-30% in Becker's and to about 15% in our studies. For the spectrally integrated I_0- ratio Becker et al report 15.2 which represents a considerable, further increase over a value of about 12.5 at their lowest measured pressure of 0.2 millitorr. This leads them to set $I_0^O = 4.2 \times 10^{-18}$ cm³ molecule⁻¹ sec⁻¹ for the rate constant of the purely two-body process by normalization to the high pressure I_0 of 6.4×10^{-17} by Fontijn et al[3]. Although all of our data have not yet been fully analyzed, we would favor an integrated I_0- ratio in the 10-12 range.

A spectral M-dependence was first seen qualitatively by Freedman and Kelso[15] at high pressures, and recently in much greater detail by Becker et al[11]. In terms of the energy transfer mechanism, such a dependence of spectrally resolved fall-off curves on M is, of course, absolutely required if a total,

integrated M-effect exists as the data in Table I seem to indicate. Since the residual, low pressure, truly bimolecular emission process can not depend on M and must therefore be identical in all gas mixtures, this high pressure M-effect suggests different efficiencies for vibrational energy transfer for different M in such a way that an M for which R in Table I is greater than 1 (such as He) should have larger spectrally resolved fall-off ratios in the red, and an M such as SF_6 should have smaller ones. Thus, ref. 11 reports a $I_0^\lambda(p\to\infty)/I_0^\lambda(p\to 0)$ of 8.45 for CO_2 and 5.8 for SF_6 at 5600Å compared to 10.5 for O_2, but one of 17.2 for He at 6320Å compared with 13.5 for O_2. The mechanistic picture appears to be entirely consistent with the available experimental data.

B. 4. The Temperature Dependence

The temperature dependence has been experimentally studied only at high pressures, first by Clyne and Thrush[13] between 200 and 300°K who reported, for $M=O_2$, $I_0^\infty = 5 \times 10^{-18} \exp[(1500 \pm 400)/RT]$ cm^3 $molecule^{-1}$ sec^{-1} or an analogous T^{-n} expression of $6.4 \times 10^{-17} (T/300)^{-3\pm 0.8}$. Hartunian et al[16] covered the range 500 - 1200°K in their glow discharge shock tube experiments and reported a somewhat lesser negative temperature dependence of $T^{-1.55}$ in T^{-n} form but a somewhat larger exponential dependence of $\exp(2200/RT)$. Parkes[17] studied the temperature dependence for $M=O_2$, He, Ar, CF_4, and SF_6 at 1.5 torr from 170 to 370°K in a simple, yet accurate flowtube experiment with three matched photomultiplier tubes of which one viewed the chemiluminescence at a position whose temperature was varied, while the other two simultaneously measured the intensity at 300°K up-and downstream of that position. This provided accurate intensity ratios as the temperature of the center section was varied slowly and continuously. Neither a pure T^{-n} nor an $\exp(E/RT)$ gave a fully satisfactory fit, but a two parameter expression $T^{-m} \exp(-300/RT)$ provided a good description with

m=2.50 for O_2, 2.65 for He and Ar, and 1.90 for CF_4 and SF_6, which predicts that in the 900 to 1200°K range the emission will have equal intensity for all 5 M-gases. This effect can be qualitatively ascribed to the increasing probability of re-excitation of vibrationally quenched NO_2^* at higher temperatures and to unequal energy increments in the vibrational ladder.

Vanpee et al[18] recently reported a new measurement of the integrated rate constant I_0^∞ of 6.8 x 10^{-17} cm^3 molecule^{-1} sec^{-1} ± 35% for M=O_2 and N_2 in a free jet at 367°K at pressures near 1 torr. They also reported a greater contribution of near infrared radiation to the spectrum which is responsible for a 12% increase in the spectrally integrated I_0^∞ under otherwise identical conditions. With this correction and the above temperature dependence measured by Parkes[17], a value of (9.3 ± 3.2) x 10^{-17} is obtained for comparison with that of (6.4 ± 1.9) x 10^{-17} of Fontijn et al[3] at 296°K.

B. 5. Infrared Measurements

The absolute intensity measurements of Fontijn et al[3] extended to 1.4μm where the signal was found to be negligible, but this was primarily a detectability problem. Since then, the infrared chemiluminescence and vibraluminescence has been studied by Stair and Kennealy[19] who measured the emission spectrum to 7μm using Fourier interferometer spectroscopy and found a considerably stronger infrared component of the emission than the earlier workers. I_0^∞ decreased about 20 fold from 1.25 to 3.3μm, but then increased about 3 fold to a peak at 3.7μm and fell sharply to near zero at 4.0μm. Vanpee's[18] spectral measurements to 2.0μm are in qualitative agreement with the more extensive work of Stair and Kennealy, but they indicate a somewhat too great intensity decrease between 1.2 and 2.0μm. Roche and Golde[20] in my laboratory are now doing absolute intensity measurements using liquid nitrogen cooled PbS and InSb detectors and a circularly variable
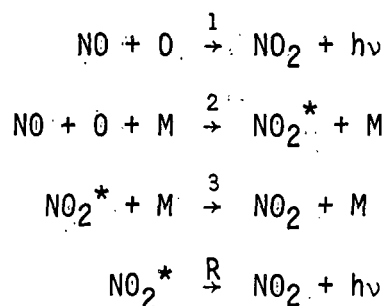
filter for spectral dispersion. Preliminary results at total pressures from 0.3 to 3 torr are in good agreement with Stair's results on the spectral distribution including the peak at $3.7\mu m$ and suggest a larger absolute rate constant in the overlapping 1.0 to $1.5\mu m$ range than either Fontijn or Vanpee.

C. DISCUSSION AND INTERPRETATION

C. 1. The NO_2^* Energy Transfer Model

It is clear from the preceding sections that either simultaneous two-body and three-body recombination (Model I) or the two-body formation of an unstabilized NO_2^* collision complex followed by vibrational, electronic, and radiative processes (Model II) can be used in the interpretation of experimental data. Model I can be set down as follows:

$$NO + O \overset{1}{\rightarrow} NO_2 + h\nu$$

$$NO + O + M \overset{2}{\rightarrow} NO_2^* + M$$

$$NO_2^* + M \overset{3}{\rightarrow} NO_2 + M$$

$$NO_2^* \overset{R}{\rightarrow} NO_2 + h\nu$$

which, with NO_2^* in steady state, yields
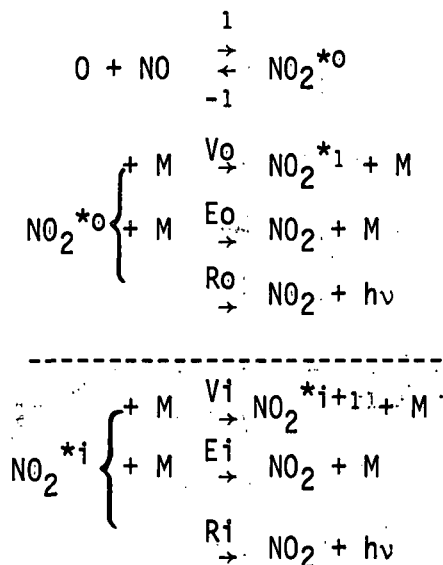
$$I_0^M = k_1 + \frac{k_2 k_R [M]}{k_R + k_3 [M]} \qquad (1)$$

with limiting values $I_0^M(p \rightarrow 0) = k_1$ and $I_0^M(p \rightarrow \infty) = k_1 + (k_2 k_R/k_3)$ i.e. a fall-off ratio of $1 + (k_2 k_R/k_3 k_1)$. Although [M] has cancelled out in this expression, the fall-off is, of course, M-dependent, since the rate constants k_2 and k_3 will be different for different M, and should perhaps have better been labelled k_2^M and k_3^M. In this, its simplest form, Model I is unsatisfactory as most Stern-Volmer type models, because it recognizes only a single energy level

in the excited state and can therefore not explain spectral shifts due to p or M.

In this form it may be compared with Stern-Volmer data on NO_2 fluorescence quenching[21], and the second term of eq. 1 can be re-written $k_2[M]/(1+a[M])$ where $a = k_3/k_R$ is the quenching constant, on the (unreasonable) assumption that the same single excited state is reached in both processes. Model I can now be generalized by allowing for a large number of levels in NO_2^*, summing over all of their steady state concentrations and introducing k_{2i}^M and k_{3i}^M as well as k_{Ri}. With that number of adjustable parameters, one could, of course, explain the spectral p and M dependence as well as pressure fall-off plots as complex as the silhouette of a giraffe or the oboe part of the first movement of Beethoven's Seventh. Yet, some physical unreasonableness would remain in this complicated model, since it would require that all levels of NO_2^* have to be formed and quenched in single collisions, no matter how large the energy gap between them and the NO + O continuum or the NO_2 ground state, i.e. it retains the "strong collision" approximation.

Model II relies on a stepladder process of vibrational energy transfer:

$$O + NO \underset{-1}{\overset{1}{\rightleftarrows}} NO_2^{*0}$$

$$NO_2^{*0} \begin{cases} + M \overset{Vo}{\rightarrow} NO_2^{*1} + M \\ + M \overset{Eo}{\rightarrow} NO_2 + M \\ \overset{Ro}{\rightarrow} NO_2 + h\nu \end{cases}$$

$$NO_2^{*i} \begin{cases} + M \overset{Vi}{\rightarrow} NO_2^{*i+1} + M \\ + M \overset{Ei}{\rightarrow} NO_2 + M \\ \overset{Ri}{\rightarrow} NO_2 + h\nu \end{cases}$$

where the collision complex, NO_2^{*0}, is capable of rapid redissociation, k_{-1}, in addition to three other modes of transformation, V (vibrational energy transfer), E (electronic energy transfer), and R (spontaneous radiation). If now, in the simplest approximation, all V_i are set equal, $V_i = V$, all $E_i = E$, and all $R_i = R$, the steady state approximation is applied to all NO_2^{*i}, and (very reasonably) $k_{-1} \gg (V[M], E[M], R)$, (to avoid having a flood of subscripted k's, the rate constants are labelled V, E, and R), one obtains, setting $k_1/k_{-1} \equiv K$,

$$I_0(p) = KR \left[1 + \frac{1}{1+S+X} + \left(\frac{1}{1+S+X}\right)^2 + \cdots \left(\frac{1}{1+S+X}\right)^n \right] \qquad (2)$$

where $S \equiv E/V$, $X \equiv R/(V[M])$, and n is the number of vibrational levels which are able to radiate at a given emission wavelength, i.e. $n=1+(\nu_0-\nu_\lambda)/\Delta\nu_V$ with $\nu_0=25,160$ cm^{-1}, the full O + NO bond energy, ν_λ the reciprocal of the emitted wavelength, and $\Delta\nu_V$ the average vibrational energy (cm^{-1}) transferred per collision with M. It must be pointed out that, in addition to all other simplifications, eq. 2 neglects the spectral difference of the I_0^i contributions coming from the different NO_2^{*i} and therefore does not explicitly show the spectral pressure shift. As $p \to \infty$, $X \to 0$, so that the model predicts $I_0^\lambda(p \to \infty)/I_0^\lambda(p \to o)$ ratios to equal $1 + 1/(S+1) + \cdots$ $1/(S+1)^n = (1-B^{n+1})/(1-B)$ where $B = 1/S+1 = V/(E+V)$, and, for $n \to \infty$ the ratio approaches $1 + (V/E)$.

Model II was first proposed by Keyser, Kaufman, and Zipf[22] on the basis of NO_2 fluorescence studies in which E and V were fitted to data on monochromatic, steady excitation of NO_2 with monochromatic fluorescence intensity measurements, and R was measured by the phase shift method using modulated excitation[23]. As applied to the O + NO chemiluminescence, it predicted surprisingly accurately the now experimentally observed fall-off ratio of about 10 for the spectrally integrated, high pressure emission rate constant, I_0^∞, to its low pressure limit,

I_0^O. It was also used by Becker et al[11] to extract information on the magnitudes
of E, V, and $\Delta\nu_V$ from their fall-off data, i.e. $E \simeq 2x10^{-12}$ cm^3 molecule^{-1} sec^{-1},
$V \simeq 2x10^{-10}$ cm^3 molecule^{-1} sec^{-1}, and $\Delta\nu_0 \simeq 800$ cm^{-1}, based on a radiative life-
time of 60μsec for NO_2^*. Similar analysis of Cody's[12] data appears to give
$V = (1$ to $2) \times 10^{-10}$, $E \sim 1x10^{-11}$ cm^3 molecule^{-1} sec^{-1} and $\Delta\nu_V \sim 500$ to 1000 cm^{-1}.
The model does, of course, correctly predict the decreasing values of the spec-
trally resolved fall-off ratios (see Table II) at lower λ, because as λ is
decreased so is n, the number of NO_2^{*i} levels which are able to emit, and thereby
the number of contributing terms in eq. 2.

In its above form, Model II assigns equal statistical weights to the
vibrational states of NO_2^*, which is unreasonable, because with three oscillators
there is a higher density of states at higher energy. Schwartz and Johnston[24]
introduced an RRK statistical weight, $g_j = (j+s-1)!/j!(s-1)!$, with j = total
number of average vibrational quanta (set equal to 1250 cm^{-1}) above the origin
of NO_2^* (set equal to 12,500 cm^{-1}) and s=3, in their study of NO_2 fluorescence.
For NO_2^* states near the 0 + NO continuum, j therefore equals 10 and g_j=66,
whereas the equivalent g_j for ground state NO_2 (j=20) equals 231, and by coming
down 5 vibrational steps (which is equivalent to going from about 4000 to 5300Å
in emission threshold) g_j would decrease to 21 in NO_2^* and to 105 in the ground
state. In future calculations this effect, which will tend to deplete higher
energy levels faster than lower ones, should be included and g_j calculated more
realistically.

The experimentally fitted parameters, V, E, and $\Delta\nu_V$ are in surprisingly
good agreement with the results of two fluorescence studies,[23,24] although it
is puzzling (a) that for M=O_2 $\Delta\nu_V$ should be in the range 500 to 1000 cm^{-1} when
$\nu(O_2)$ = 1580 cm^{-1}, and (b) that the energy transfer rate to O_2 would still be
nearly gas-kinetic. On the whole, however, the physical picture is remarkably

consistent, and has good predictive power with an economical minimum of assumptions and adjustible parameters. It requires only a single electronically excited state which it reasonably assumes to be identical with that reached in fluorescence, and, using its known (average) lifetime, interprets all aspects of the radiative recombination in terms of an energy transfer model which has had many successful applications in simple, non-radiative processes. We may be tempted to stop here and bask in its simple glory, but there are promises to keep, and miles to go before we sleep.

C. 2. Connections with NO_2 Spectroscopy, Fluorescence, Photodissociation and Quantum Calculations

Before we launch into this general discussion, a few experimental facts:

(1) The absorption spectrum of NO_2 in the visible from 4000 to 8000Å is amazingly complex, and has, with the exception of a band progression near 4000Å which Douglas and Huber[25] showed to arise from a $^2B_1 \leftarrow ^2A_1$ transition, resisted analysis, even at 1.5°K.[26] Discrete features of the resonance fluorescence spectrum of NO_2 excited at 5145Å with an argon ion laser were analyzed by Abe, Myers, McCubbin, and Polo[27] and ascribed to a $^2B_2 \leftarrow ^2A_1$ transition. Still more recently, Stevens, Swagel, Wallace, and Zare[28] have analyzed the fluorescence spectrum excited at 5934 to 5940 Å by a narrow band, pulsed, tunable dye laser and report features due to both $^2B_1$ and $^2B_2$ states.

(2) The extensive quantum calculations of Gangi and Burnelle[29] indicate that the two lowest excited states of NO_2, $^2B_1$ and $^2B_2$, lie 1.75 and 3.33 eV above the $^2A_1$ ground state in its equilibrium configuration and that their radiative lifetimes, τ_R, are 1.53 and 0.125 μsec, respectively. Of the next three states, $^4B_2$, $^4A_2$, and $^2A_2$, only the $^4A_2$ state has an appreciable transition probability to the ground state corresponding to a τ_R of 8 μsec. The $^2B_1$ state

has a linear or nearly linear equilibrium configuration and the $^2B_2$ state is more strongly bent than the ground state ($\sim$110°).

(3) Photodissociation studies of NO_2 at 3471Å by Busch and Wilson[30] have shown that the rapidly dissociating (or predissociating) state reached in the initial absorption is predominantly of B_2 symmetry. Their upper limit of $\sim$2 x 10^{-13} sec for the dissociation lifetime is in good agreement with the results of high pressure photolysis experiments by Gaedtke, Hippler, and Troe.[31]

(4) Finally, we must consider the increasing number of partly contradictory fluorescence lifetime studies and their relevance to the air afterglow. Ever since Neuberger and Duncan's[32] direct measurement of 44μsec for τ_R, the discrepancy between that value and 0.26μsec calculated from the integrated absorption coefficient has been under experimental and theoretical scrutiny. The experimental search for a second, very much faster state gave uniformly negative results[23,24,33] with the exception of recent indications[34] that a very small fraction of the total emitted fluorescence may have a shorter lifetime (0.5 to 3.7 μsec) at a few wavelengths. This observation, even if correct, does, of course, in no way help to bridge the lifetime anomaly. Surprisingly, then, at least six studies[23,24,32,33,35,36] are in broad agreement that the measured lifetime is in the 60 to 70 μsec range when viewing geometry corrections are applied[23,24,35], although a minor controversy remains whether τ_R remains essentially constant[23] over the 4000 to 6000Å excitation range or exhibits fairly discontinuous variations of 10 to 20% when the excitation band width is narrowed to 1 to 5 Å. Only the recent findings of Zare's group[28] of non-exponential decays in the unresolved fluorescence at 5934.5Å, which is then spectrally resolved into stronger features coming from a $^2B_2$ state with τ_R = 30 ± 5 μsec and weaker features believed to be coming from a $^2B_1$ state with τ_R = 115 ± 10 μsec, are in some conflict with the other data, but although such

experiments are clearly most important and desirable, they will have to be repeated for an extremely large number of lines in the complex NO_2 absorption spectrum before conclusions may be drawn about their importance in the overall process. It is significant to note that four of the above six lifetime studies[23,32,33,35] directly or indirectly looked for non-exponential behavior and found either none or very little.[35]

The extent to which the lifetime anomaly is explainable in terms of well-known physical processes was characterized very clearly by Douglas[33] who suggested four independent causes, the v^3 frequency effect, transition moment variation with internuclear distance, vibrational level mixing, and interelectronic state mixing. Of these, the first may contribute small factors, e.g. excitation (or recombination) at an effective excitation wavelength of 4000Å and radiation at 6000Å provides for a factor of 3.4; the second is difficult to assess, but is unlikely to be large, at least by analogy with the behavior of diatomic molecules; the third, although surely applicable in NO_2 whose vibration frequencies are low and whose excited states have substantially different equilibrium geometries from the ground state, is more likely to help explain the very complex absorption spectrum, because each band is spread into overlapping weaker bands, than the lifetime anomaly except again through the v^3 and R_e effects; it seems, therefore, that interelectronic state mixing must supply the bulk of the total factor of nearly 300 which needs to be rationalized, i.e. a factor of 30 to 100. Two prerequisites must then be fulfilled: (a) the states must interact strongly, and (b) their level density ratio must be sufficiently large. The second of these requirements, in conjunction with the known energetics of all possible states,[29] strongly points to the ground state as the cause of the perturbation, i.e. both in fluorescence and chemiluminescence, vibrationally highly excited $NO_2(X^2A_1)$ may be strongly

mixed with the $^2B_1$ and $^2B_2$ states. For $^2B_1$, the interaction can not be vibronic, as there are no vibronic symmetry species common to both states, but may be due to Coriolis interaction. The latter will increase strongly with increasing rotational energy, but may not be sufficiently strong to provide the extensive mixing which is required. For $^2B_2$, vibronic interactions are possible.

In the absence of detailed information on the vibration frequencies of the two excited states, no quantitative estimates of level density ratios can be made, but certain limiting approximations provide useful information. At the high levels of vibrational excitation, at least for the ground state, the semiclassical expression of Marcus and Rice[37] $N(\varepsilon)=(\varepsilon+\varepsilon_z)^{s-1}/[\Gamma(s)\overset{s}{\Pi}h\nu_i]$ should be applicable. Here ε_z is the total zero-point energy and s, the number of oscillators, equals 3. For $NO_2(X)$, $\varepsilon_z=1850$ cm^{-1} and since ε values of 15,000 to 25,000 cm^{-1} are of interest here, ε_z may be neglected. If it is further assumed that excited state frequencies are roughly equal to those of $NO_2(X)$, the level density ratio is given by $(\varepsilon/\varepsilon')^2$ where ε and ε' are the total vibrational energies of the ground and excited states. If the frequencies are not equal it will be more likely that the excited state frequencies will be lower than those of the ground state, and in that case, the N/N' ratio will be less than $(\varepsilon/\varepsilon')^2$. Now, for the $^2B_1$ state, both experiment and theory put its energy minimum at or below about 12,000 cm^{-1} (corresponding to an origin of the $^2B_1\rightarrow^2A_1$ band system at or beyond 8000Å) which, at excitation frequencies (or recombination energy) of 20,000 to 25,000 cm^{-1}, will make $\varepsilon/\varepsilon'\lesssim2$ and the level density ratio $\lesssim4$, i.e. far too small to explain the lifetime anomaly. For the higher lying $^2B_2$ state the situation is somewhat better, since its energy minimum is calculated[29] to be about 2.2 eV above that of the ground state which, depending on excitation frequency, may give ε/ε' in the 3 to 10 range and corresponding density ratios of 10 to 100. The danger and

possible fallacy of this argument is, however, that, particularly in the excitation range where N/N' is large, its magnitude is primarily controlled by that of N' which is decreasing rapidly as the origin of the $^2B_2\text{-}^2A_1$ band system is approached and one would therefore predict a strong dependence of observed fluorescence lifetime on excitation frequency, i.e. an increase of τ_R up to about 6000Å, and a sharp decrease beyond that wavelength. Schwartz and Johnston[24] did report a small increase of τ_R in the excitation wavelength range from 4000 to 5600Å and a small decrease from there to 6000Å, but our own work did not support even these minor trends and showed τ_R to be constant.

Nevertheless, it would be interesting to measure τ_R in the low pressure limit as far into the red as possible. On the whole, the fluorescence lifetime anomaly seems less resolved than ever, even though the great complexity of the absorption and emission spectrum comes as no surprise. The weakness of the level density argument has all but eliminated one of the principal potential explanations, the pseudo-degeneracy of the upper state by mixing with excited ground state.

The implications of this large body of related work for the $O + NO$ afterglow are unclear. The $^2B_1$ is favored as the emitter by its direct correlation with $O(^3P) + NO(^2\pi)$ whereas the $^2B_2$ state can be reached only through an intermediate state in a pre-association for which Burnelle et al[29] have suggested a high-lying $^2A_1$ $(^2\Sigma_g^+)$ state as a likely intermediate. Carrington[38] points out that, since the recombination proceeds by way of highly unsymmetrical configurations of NO_2, i.e. in C_s rather than C_{2v} symmetry, the $^2A'$ state corresponding to $^2B_2$ may possibly be reached directly. The fact that the spectral onset of chemiluminescence corresponds closely to the full O-NO bond energy makes it unlikely that the curve crossing occurs appreciably below the continuum threshold. The smoothness of the emission

spectrum, on the other hand, argues (weakly) against invoking both excited states as does the success of the earlier parametric representation of experimental data.

The very large vibrational relaxation rate constant suggests that the role of rotational excitation in the collision complex and subsequent rotational relaxation also be considered. In their recent high pressure photolysis studies of NO_2, Troe and co-workers[39] have been able to measure the limiting high pressure, second-order rate constant for the total 0 + NO reaction, $k^\infty = 2 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}, which includes all initial recombination pathways and is therefore an upper limit to k_1 in Model II. This k^∞ corresponds to a maximum impact parameter of 1Å for collisions of spherical particles and even when allowance is made for the exclusion of wrong end collisions of NO, the impact parameter is unlikely to be larger than 2Å which means that rotationally highly excited NO_2^* will not be an important intermediate.

Lastly, the question to what extent recombination to form NO_2^* is distinct from the known overall three-body recombination process may be examined semi-quantitatively. Assuming R to be constant and equal to 1.6×10^4 sec^{-1}, and KR, the low pressure limit for I_0, to be 5 to 6×10^{-18} cm^3 molecule^{-1} sec^{-1}, $K = k_1/k_{-1}$ equals 3 to 4×10^{-22} molecule^{-1} cm^3. If, at sufficiently high pressures (≥ 0.1 torr) all NO_2^* are vibrationally relaxed with rate constants in the 1 to 2×10^{-10} cm^3 molecule^{-1} sec^{-1} range as obtained in section C.1. above, the effective three-body recombination through NO_2^* is of the order 3 to 6×10^{-32} cm^6 molecule^{-2} sec^{-1} which is in the range of the reported overall rate constants of 6 to 8×10^{-32}, i.e. the process represents a major part of the total recombination. This had been suggested by us[6] earlier in terms of the three body NO_2^* mechanism and was confirmed recently by Becker et al[11].

The molecular dissociation rate constant of unstabilized NO_2^{*0}, k_{-1}, is then ≤ 5 to 7×10^{10} sec^{-1} which is a reasonable value under thermal conditions at $300°K$ compared with the much higher 5×10^{12} sec^{-1} for NO_2^* with 10 to 12 kcal of excess energy from photodissociation[30] and high pressure photolysis[31]. The close equality of the radiative and total rate constants further supports the notion of extensive state mixing in the excited state and decreasing meaning of pure state labels. Perhaps, in desperation and exhaustion, we need not worry, then, whether $^2B_1$ or $^2B_2$ labels apply to the air afterglow emitter, because both (or more than two) are variably and complicatedly mixed with the ground state.

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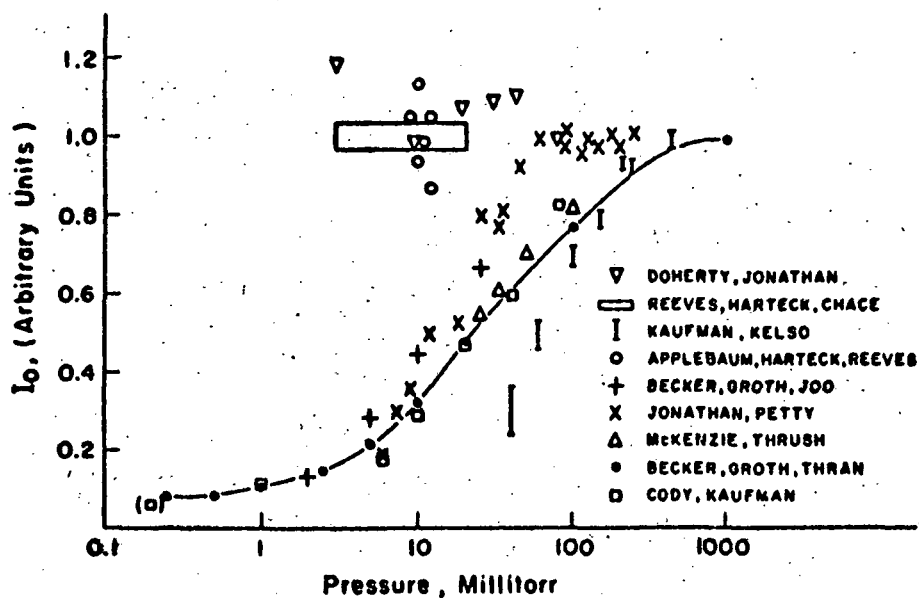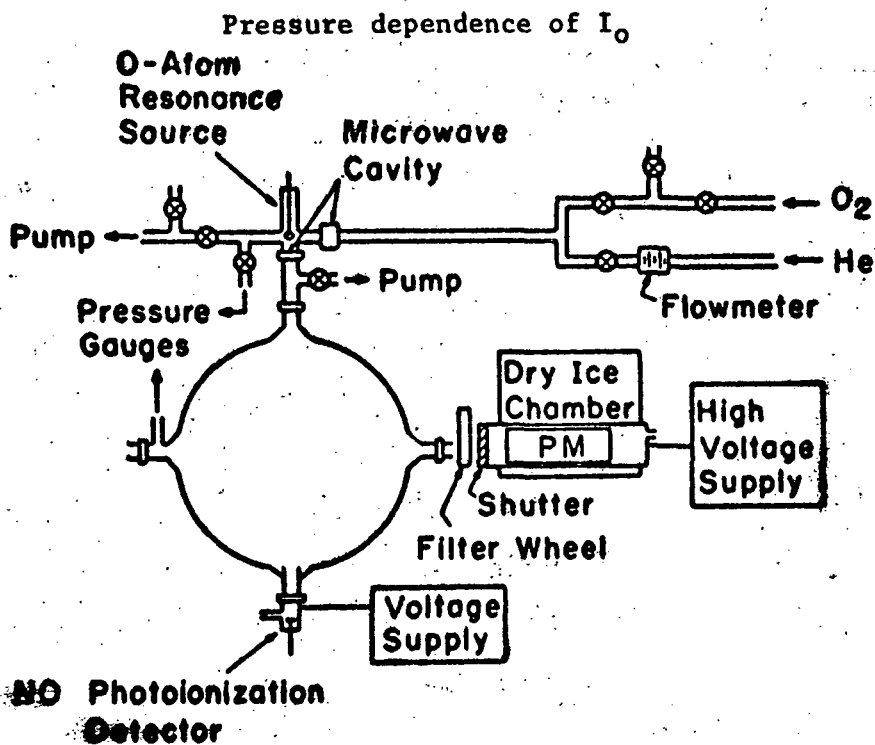
FIGURE 1

Pressure dependence of I_0

FIGURE 2

Diagram of apparatus. Top view looking down along axis of 15 cm diameter flow tube.

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13 ABSTRACT

Past and present experimental work on the $O + NO$ chemiluminescence is reviewed, conclusions are drawn regarding the pressure and M-dependence of its radiative rate constant, and a stepladder mechanism for the vibrational relaxation of electronically excited NO_2 is proposed and fitted to the data. The results are then interpreted in view of related work on the spectrum, photodissociation radiative lifetime, and quantum chemistry of NO_2^*.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Chemiluminescence;						
O-atom;						
NO						
NO$_2$						
Raditive Lifetime						
Energy Transfer						
Fluorescence						
Pressure Dependence						